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X-ray K-Emission Spectroscopy and its Application to Oxides and Silicates

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The present state of our knowledge on x-ray K-emission spectroscopy as applied to oxides and silicates has been reviewed and the works to be done, especially, for elucidation of structure of silicate glasses have been suggested.

I. INTRODUCTION

It is known that short range order of atomic arrangement is quite important in determining various characteristic properties of solid substances; a wide variety of interesting properties such as laser action, semiconduction, metallic conduction and superconductivity are realized[1] in vitreous (glassy) solids which have no long range order. "Short range order", a geometrical concept including valence and co-ordination of atoms, interatomic distance and bonding angle, is directly related to chemical bonding or electronic structure of atoms in the substance; the former determines the latter and vise versa.

In order to obtain informations on short range order in vitreous solids for which x-ray or electron diffraction structure analysis is not so effective as for crystals with a periodic lattice (only radial distribution analysis is possible for vitreous solids and this method is accompanied by a considerable error[2]), IR spectroscopy,[3] ESR and NMR methods,[4,5] optical absorption and emission[6] and Mössbauer method[7] are applied, depending upon the atomic species considered. These methods characterize materials by providing us with informations on the electronic state of a given atom and the structure of its immediate vicinity. X-ray emission spectroscopy has been paid attention to as one of such methods of characterizing materials.

In the present paper x-ray K-emission spectroscopy will be reviewed with particular emphasis on the results as to oxides and silicates, both crystalline and glassy. Experimental procedures and theories and interpretations are also reviewed, however, so that more general features of K-emission spectroscopy could be understood.

II. BASIS OF X-RAY K-EMISSION SPECTROSCOPY

There are two branches of x-ray spectroscopy, x-ray absorption spectroscopy and x-ray emission spectroscopy.[8,9] An x-ray photon is absorbed by an atom, if the photon has a sufficient energy to eject an electron from an inner electron-shell of the atom. In K-absorption processes, where K electrons are involved, some minimum energy is

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required to eject a K electron into the first available higher energy unoccupied orbital. When the energy of the incident x-ray photons just equals this minimum value, a sharp rise in the absorption coefficient takes place, giving the K-absorption edge. If there is a succession of discrete energy levels in an atom to which the ejected electron can transfer, then a succession of discrete maxima should appear in the absorption curve at corresponding energies. Thus the fine structure near the x-ray absorption edge displays the distribution of normally unoccupied electron orbitals in the atom, and this forms the basis of x-ray absorption spectroscopy.

On the other hand, x-ray emission spectra correspond to electron transitions from occupied orbitals to the momentary vacant orbital created in an inner shell. When an electron has been ejected from the K shell, for example, the atom is in the excited state and one of the electrons at the outer orbital falls into the vacancy created in the K shell. In this process an x-ray photon is emitted. Thus an atom gives rise to an x-ray spectrum characteristic of the energy levels or distribution of the occupied orbitals. This is the basis of the x-ray emission spectroscopy.

As is well known, the allowed energy levels can be described in terms of the shells (K, L, M, and so on) and symmetries (s, p, d, and so on) of the electron orbitals. Combinations of permitted transitions between various states, as shown in Fig. 1, give the characteristic spectrum lines.

Generally speaking, the energy levels involved in the transitions are at the inner shells and there is little effect of chemical bonding of the atom, that is, x-ray spectrum of an element does not depend so much on whether it is free or chemically bound in a compound or whether it is in the liquid or solid state. This fact is utilized in analytical chemistry by x-ray fluorescence and electronmicroprobe methods.[8,11]

Detailed examination of x-ray spectra indicated, however, that they undergo chemical effect, slight but measurable if precise measurement is made. Shift of the

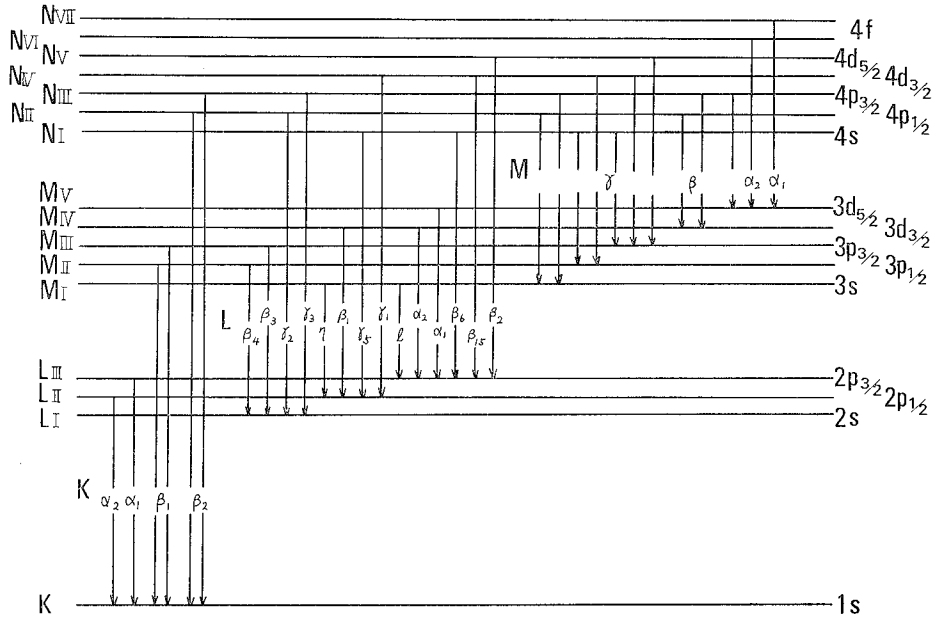

Fig. 1. Series of electronic transitions.[8,10]

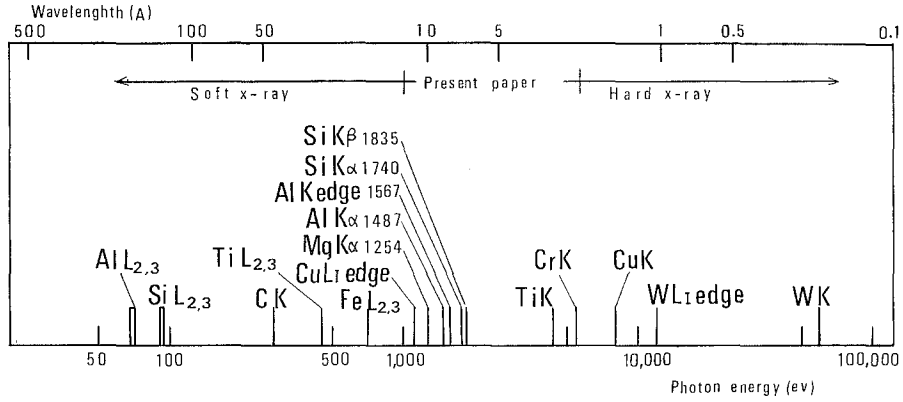

Fig. 2. Photon energies and wavelengths of various emission x-rays, illustrating the region pertinent to the present discussion.

peak (chemical shift), change of the peak shape and formation of new peaks occur. It has been known since the early 1920's that modification of the electronic structure of an atom due to compound formation is manifested by the x-ray spectrum of that atom.[12] Because a quantitatively rigorous theory to explain the x-ray spectra has not as yet been developed, experimental results on inorganic and organic compounds have been used mainly to identify the oxidation state and co-ordination of atoms in an unknown matrix by comparing their spectra with those of the atoms in a known state. At present, such treatment called fingerprinting is still important, particularly for glasses.

Compounds of light elements in the third period, such as Mg, Al and Si, are of particular significance in glass technology as well as in ceramics and minerals. K-absorption spectroscopy of the oxides of these elements requires inconveniently thin sample foils that may not be representative of bulk materials, whereas the K-emission spectra of these oxides can be obtained easily with bulk materials.[13] The ejection of an inner K-electron induces a spectrum of $K\alpha$ and $K\beta$ bands resulting from $L \rightarrow K$ and $M \rightarrow K$ electronic transitions, respectively.

In Fig. 2, approximate photon energies and wavelengths of various x-rays are given to demonstrate the x-ray region treated in the present paper.

III. ON EXPERIMENTAL METHOD

The procedure of the emission spectroscopy consists of (1) generation of x-ray emission by x-irradiation (x-ray fluorescence excitation) or by electron bombardment (primary excitation), (2) analysis (resolution) of emitted x-rays by crystal, (3) detection of x-ray emission lines and (4) analysis of the recorded emission spectrum.

According to the way of generating x-ray emission, two different instruments are available, x-ray fluorescence spectrometer and electron microprobe x-ray spectrometer. In the former case interaction of incident x-ray photons with electrons in the atoms is weaker than in the latter and, in addition, the incident x-ray beam cannot be focused

Table 1 Comparison between the Two Excitation Methods Used for X-Ray Emission Spectroscopy

	Fluorescence excitation	Primary excitation	Remarks
Spectrometer	X-ray fluorescence spectrometer	Electronmicroprobe x-ray spectrometer	Commercially Available
Excitation source	X-ray	Electron beam	
Intensity of emitted x-ray	Low	High	Spectrum can be obtained in a short time in primary excitation.
Sample size	Large 10–40 mm diameter	Small 50–300 μ diameter	Very small samples or minor inclusions can be examined in primary excitation.
Effect of irradiation	Almost no effect (discoloration)	Heating and charge storage	Change of composition during analysis such as reduction, decomposition and decrease in alkali concentration may occur in primary excitation.
Penetration of the exciting radiation	Deeper	Shallow	Bulk state is examined in fluorescence excitation. Study of thin surface layer is possible in primary excitation.

on a small spot without loss of intensity. These result in a relatively low efficiency in x-ray emission.

The two methods are compared in Table 1. It is seen that the primary excitation is very efficient and can be applied to very small samples with a shorter experimental time.[14] There is, however, an advantage in the fluorescence method which is important particularly for the study of glasses. In the electron excitation, a non-conductive sample, upon bombardment with electron beams, is overheated and also subjected to storage of electronic charge, even though a conductive film of carbon or aluminum is applied on the surface of the sample. As a result, reduction of ions, *e.g.*, change of Ti^{4+} to Ti^{3+} may happen. It is reported that even SiO_2 slowly decomposes upon electron bombardment.[15] The most pronounced effect is seen in the case of alkali-containing glasses[16]; alkali content at the spot of electron beams changes with time of irradiation. This change is reflected upon the relative contents of the other elements and affects the shape of the emission peaks of, for example, Al, Si and Mg in the glass. No such effect is seen in the fluorescence method. Therefore, the emission spectroscopy of glasses should be conducted by the fluorescence method, or a great care (careful calibration) should be taken to avoid misinterpretation of data if the electron microprobe instrument is used.

For details of experiment with electron microprobe instrument, a paper of Dodd and Glen[13] can be referred to. A large defocused electron-beam spot of the order of 50 to 400 μ in diameter is employed in order to minimize the problem of overheating. Resulting deterioration of spectrometer performance can be compensated by using a small exit slit in front of the detector. Detector is an argon-filled, sealed proportional counter. Pulse height analysis is employed. To record data, x-ray spectrometer is scanned at 0.02 Å/minute. A constant electron beam potential of 20 kV is used. Instrumental resolution of the microprobe spectrometer is of the order 1.0 to 1.5×10^3

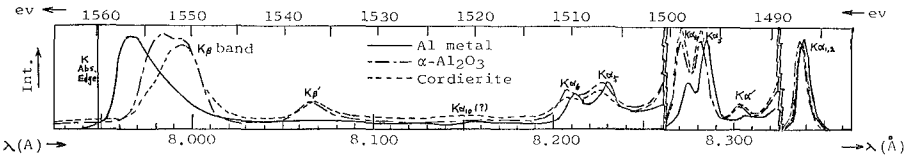

Fig. 3. Complete K-emission spectra of aluminum, showing spectra of metal, sixfold-coordinated oxide (α-Al_2O_3) and fourfold-coordinated oxide (cordierite) (Dodd and Glen).[13]

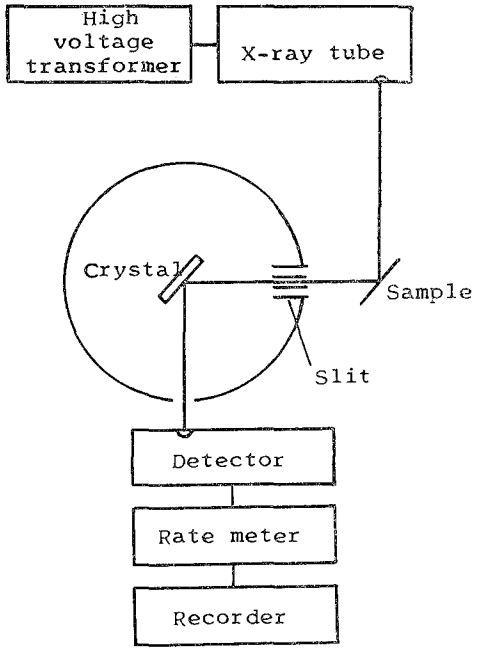

Fig. 4. Simplified block diagram of an x-ray fluorescence spectrometer.

when measured by Rayleigh's criterion, $\lambda/\Delta\lambda$. By the way, the half-width of the Alk$\alpha_{1,2}$ line is about 0.01 Å at a wavelength of 8.34 Å. Samples of metals and oxides mounted in polyacrylic metallurgical mounts and polished are coated in an evaporator with a carbon or beryllium film, about 200 Å thick. A complete K-emission spectrum of aluminum determined under the above condition is reproduced in Fig. 3.[13]

In the fluorescence excitation method, an x-ray fluorescence spectrometer manufactured for chemical analysis of elements is used with additional precautions.[17-19] A simplified block diagram of the spectrometer is shown in Fig. 4. To produce fluorescence x-ray from light elements such as Al and Si, x-ray tube with chromium target is suitable. Control of room temperature is desirable to keep the lattice distance of monochromator crystal (*e.g.*, EDDT for AlKα) constant. Solar slit of dispersion angle 0.115° is used. The high absorption of soft radiation requires a vacuum path evacuated to 10^{-1}~10^{-2} mmHg and a suitable detector, *e.g.*, gas flow proportional counter. A pulse height analyser is used. Slow scanning rate of 1/4~1/8° (2 θ) or step scanning

is employed for recording. With these arrangements the peak position measured at half-maximum intensity can be determined to an accuracy of the order of $\pm 0.005°$.

IV. RESULTS ON MINERALS, CERAMICS AND GLASSES

It was mentioned that the K-emission spectra of Mg, Al and Si can be generated readily and presents useful informations. With elements of relatively higher atomic number the energy levels involved in the measurable emission processes (L—K transitions) are well screened by electrons of outer shells and the effect of chemical bonding is too small to be informative (the absorption spectra are useful since the outer orbitals are involved). On the other hand, with lighter elements the photon energy of emission x-ray is so small that an routine spectrometer can not be used, in spite of possible larger effect of chemical bonding. For the spectroscopy involving very soft x-rays a book edited by Fabian[20] should be consulted.

K-emission spectroscopy of Al and Si are quite important in ceramics and mineralogy, because (1) these elements are common and major components, playing

Table 2 Summary of X-Ray Emission Studies on Ceramics and Glasses

Emission	Excitation source	Compound examined	Objective of study	Reference
$MgK\beta$	Electron	MgO, $MgAl_2O_4$	Chemical bonding	13
$AlK\alpha$	X-ray	Various minerals and compounds	CN (coordination number) of Al	18
	X-ray	BaO-Al_2O_3-TiO_2-SiO_2 glass and its crystallized product	CN of Al	21
	X-ray	Na_2O-Al_2O_3-SiO_2 glass	CN of Al	22
	X-ray	Various glasses containing Al_2O_3	CN of Al	19
	X-ray	Na_2O-Al_2O_3-SiO_2 glass	CN of Al	17
$AlK\beta$	Electron	α-Al_2O_3, cordierite	Chemical bonding	13
	X-ray	Various glasses containing Al_2O_3	CN of Al	19
$SiK\alpha$	X-ray	Si, Si_2O_3, SiO_2	Presence of Si_2O_3	23
$SiK\beta$	Electron	Stishovite, quartz and fused silica	Chemical bonding	13
	Electron	45 silicate minerals	Polymerization of SiO_4 tetrahedra	24
$TiK\alpha$	X-ray	Titanium oxides and titanates	Valency of Ti, Electronegativity	25
	X-ray	BaO-Al_2O_3-TiO_2-SiO_2 glass and its crystallized product	Valency of Ti	21
	Electron	TiO, Ti_2O_3, TiO_2	Check of the method	14
$TiK\beta$	X-ray	Titanium oxides and titanates	Valency, Electronegativity, Interionic distance	25
	Electron	TiO, Ti_2O_3, TiO_2	Check of the method	14
$CrK\alpha$ + $CrK\beta$	X-ray	Cr_2O_3, K_2CrO_4	Valency of Cr	26

important roles, and (2) other methods (ESR, NMR, optical absorption *etc.*) of examining short range order can not be applied to these elements with the exception that I.R. spectra give certain limited informations.[3]

In Table 2 are summarized some pertinent works published so far. Most of the works aim at correlating peak positions with structure of compounds or at identifying coordination or oxidation state of the atom in crystalline and glassy matrices by way of "fingerprinting".

One of the most significant results on determination of coordination by the present method is that of Brindley and McKinstry[18], who confirmed the four-fold coordination (in contrast to six-fold coordination in both the end minerals) of Al atoms in metakaolin. Metakaolin is an intermediate reaction product appearing in the course of transformation of kaolinite, a layer structure, to mullite, a three dimensional network structure, by heating, and its structure has been discussed extensively.[27] Measurements were made of 2θ for the AlKα emission from metallic aluminum and from the materials containing Al ions, and the difference $\Delta(2\theta)$ was determined.

$$\Delta(2\theta)=2\theta(\text{sample})-2\theta(\text{aluminum metal}).$$

The results are reproduced in Fig. 5,[18] where $\Delta(2\theta)$ is shown for the principal minerals of the kaolin group, before and after heat treatment, and for a number of calibrating substances. In kaolinite, dickite, nacrite, halloysite, gibbsite and corundum (α-Al_2O_3), Al has sixfold coordination to oxygen and $\Delta(2\theta)$ determined lies in the range -0.09 to $-0.11°$. In $AlPO_4$ and albite (Na-feldspar), Al has fourfold coordination and $\Delta(2\theta)$ lies in the range -0.06 to $-0.07°$. Kaolin minerals dickite, kaolinite, kaolinite (disordered) and halloysite heated to 750°C for 2 hours are converted to metakaolin, and in the four cases examined $\Delta(2\theta)$ moved into the range of values corresponding to fourfold coordination. The results provide clear evidence that in metakaolin the Al ions are in the fourfold coordination.

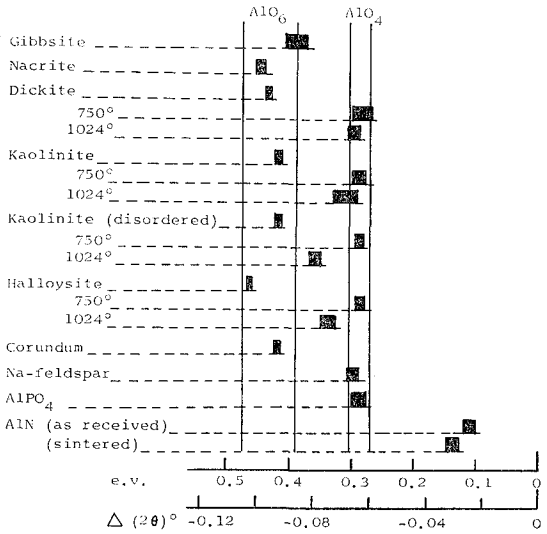

Fig. 5. Representation of $\Delta(2\theta)$ for various minerals (Brindley and mckinstry).[18]

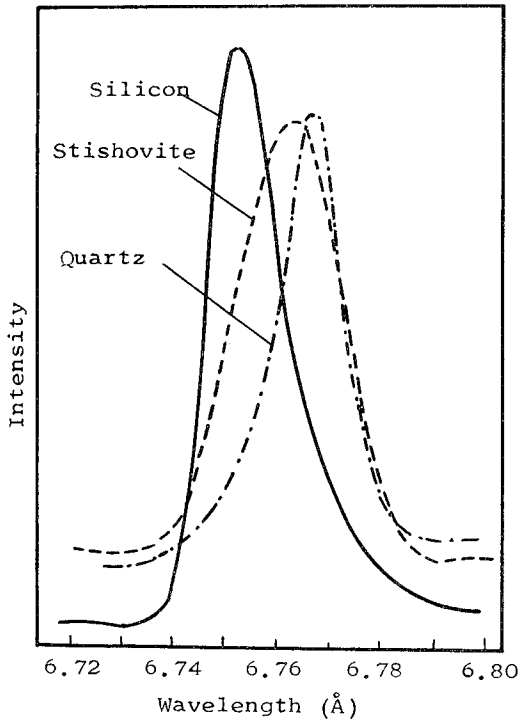

Fig. 6. The SiKβ bands from elemental silicon, α-quartz (fourfold coordination) and stishovite (sixfold coordination). (White and Gibbs).[24]

The coordination number of silicon to oxygen in oxides and silicates is well established by diffraction and other studies and usually it is four except in stishovite, a high pressure form of silica having rutile-type structure. Figure 6 shows the Kβ-emission from Si in silicon metal, low quartz and stishovite copied from a spectrum published by White and Gibbs.[24] It is seen that sixfold-coordinated oxide (stishovite) gives a distinctly different spectrum from that of fourfold-coordinated oxides (low quartz and fused silica).

It should be noted here that for Mg, Al and Si, all of the Kα diagram lines and satellites are shifted to higher energies (shorter wavelengths) for oxide, relative to the free element, whereas opposite shifts are observed for the Kβ band.[13]

Although the different coordination number gives a distinct difference to emission spectrum of the cation, detailed study allows us to obtain more informations on the environment of a given cation other than simple coordination number. White and Gibbs[24] examined the Kβ emission from Si in 45 silicate minerals using its shift as indicator. The values of the shift Δ for SiKβ, relative to the peak position for quartz, have been correlated with Si–O tetrahedral bond length. Figure 7 is a plot of Δ against mean Si–O bond length for those silicates which have only silicon in tetrahedral coordination. With the exception of zircon, the plotted points fall along a straight line within the experimental error of the measurements. Thus it appears that Δ can be used to predict the mean Si–O bond length. Considering that the mean Si–O bond

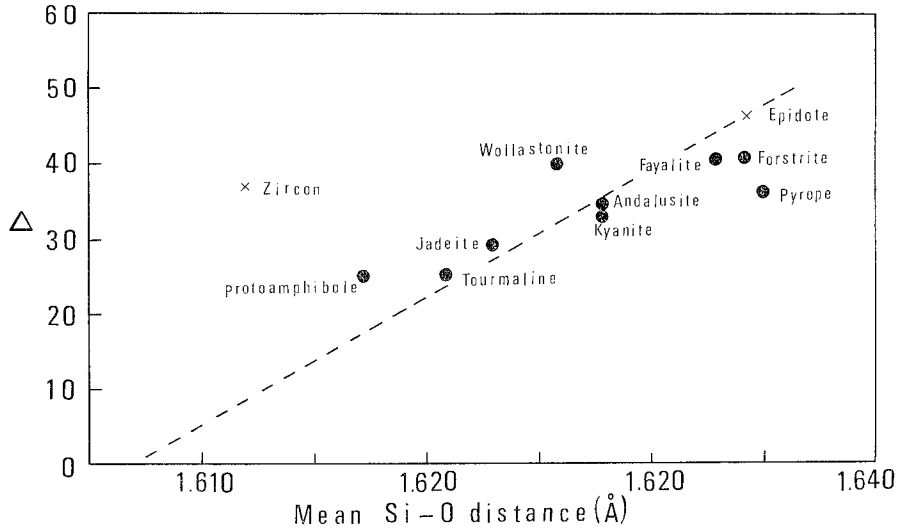

Fig. 7. Plot of ΔSiKβ versus Al/Si ratio for silicate framework structures where both the Al and Si are in tetrahedral coordination (White and Gibbs).[24]

length is closely related to structure-type of silicates, it is possible to predict the degree of polymerization of the SiO_4 tetrahedra in an unknown silicate from the Δ value.

The technique of x-ray emission spectroscopy could be effectively applied to glasses and amorphous or poorly crystallized materials, as the degree of long range order does not affect the peak shift. In glasses coordination number of cations to oxygen is very important since it determines various properties. There are a number of means for coordination determination, such as NMR for boron and optical absorption for transition metal ions. These means cannot be applied to aluminum ions, however, although many glass scientists are now interested in their coordination and arguing critically. The behavior of the Al ion is interesting partly because it is an intermediate cation from the glass-structural point of view in which the elements are classified into network-formers, network-modifiers and intermediates, according to the role in glass networks.[28] More specific problem of the coordination of Al has been recently presented[17,29,30] as to whether it changes in Na_2O-Al_2O_3-SiO_2 glasses from 4-fold to 6-fold as the Al/Na ratio exceeds unity. To solve this problem x-ray emission measurement has been attempted by a number of glass scientists[17,19,23] (see Table 2). Fluorescence method, instead of primary excitation, was used by all the three authors.

The procedure is essentially identical to that used by Brindley and McKinstry[18] for the determination of Al coordination in metakaolin mentioned above; the peak position of the AlKα emission for Al metal was measured and then the relative displacement of the AlKα peak for glasses was determined. The displacement was compared with those for minerals and compounds containing Al ions with a definite coordination number of six or four. Results obtained by Day and Rindone[22] are shown in Table 3. Their data appear to show that glasses having an Al/Na ratio equal to less than 1 contain only Al ions in fourfold coordination, while glasses having the Al/Na ratio over 1 contain a portion of Al ions in sixfold coordination. It should be noted, however, that Day and Rindone examined only a small number of reference materials for sixfold- and

Table 3 Shifts of AlKα Peak for Soda Aluminosilicate Glasses[22]

	Al/Na ratio	Displacement Glass
Glass composition		
$1.25Na_2O \cdot 0.75Al_2O_3 \cdot 6.00SiO_2$	0.60	0.022
$1.00Na_2O \cdot 0.80Al_2O_3 \cdot 2.20SiO_2$	0.80	0.025
$1.00Na_2O \cdot 1.00Al_2O_3 \cdot 6.00SiO_2$	1.00	0.022
$0.80Na_2O \cdot 1.20Al_2O_3 \cdot 6.00SiO_2$	1.50	0.037
$0.70Na_2O \cdot 1.30Al_2O_3 \cdot 6.00SiO_2$	1.86	0.045
Reference compound		
Al metal		0.000
$AlPO_4$		0.042
Al_2O_3		0.060

fourfold-coordinated Al ions. As mentioned before, coordination number is not the only factor that affects the peak position, hence the peak position of AlKα emission is different more or less for different reference materials. In addition, experimental error easily enter this type of measurement. Therefore, further precision measurements are necessary before a reliable conclusion is obtained.[17,19]

V. THEORETICAL ASPECTS

Molecular orbital interpretation of emission bands by Dodd and Glen[13] will be introduced in the first part of this section and estimation of effective charge of atoms in solids based on the peak shift[31~34] will be described in the second part.

1. Molecular orbital interpretation

As to absorption spectroscopy, Böke[35] tried to apply the atomic orbital theory to

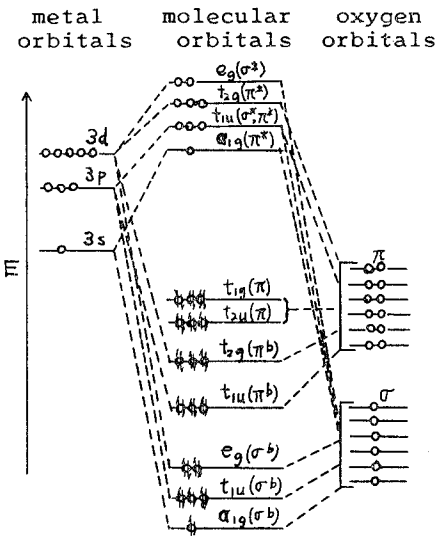

Fig. 8. Molecular-orbital energy-level diagram for octahedrally coordinated oxides of Mg, Al and Si (Dodd and Glen).[13]

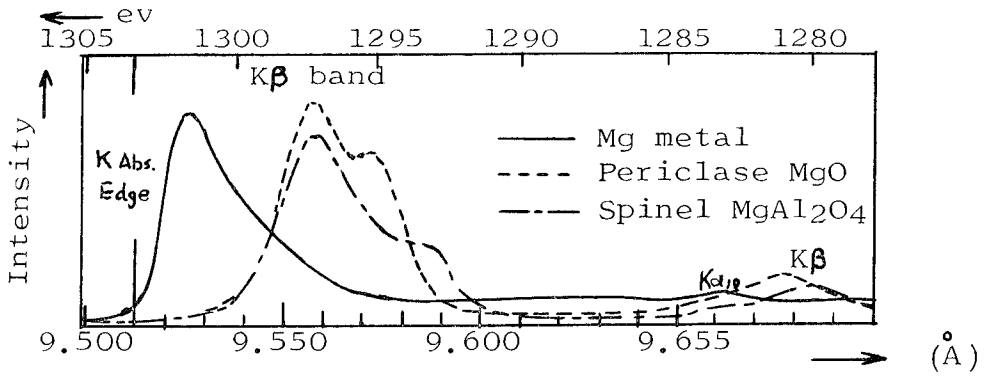

Fig. 9. Magnesium Kβ-band emission spectra of magnesium metal, periclase (MgO) and spinel (Mg Al_2O_4). Magnesium has sixfold coordination in periclase and four fold coordination in spinel (Dodd and Glen).[13]

explain the fine structure of K-absorption edges of the complex salts of elements from chromium to zinc. Band theory was considered appropriate for analysis of the abosrption spectra of metals.[36,20] Glen and Dodd[37] applied the molecular orbital (MO) theory to the K-absorption spectra of transition metal (Mn, Fe, Co) complexes.

Subsequently, Dodd and Glen tried to interpret the K emission spectra of oxides of Mg, Al and Si by MO theory.[13] Their MO interpretation of the Kβ bands (designated as M–K transition) of these elements is based on the assumption that the principal peaks in the band can be ascribed to 3p–1s transitions. Figure 8 is a tentative MO energy-level diagram for octahedrally coordinated oxides of Mg, Al and Si given by Dodd and Glen[13]. It was derived from the energy-level diagram for transition metal complexes.

In Fig. 8, the 3p (π) bonding orbitals with group t_{1u} symmetry (denoted by t_{1u} (π^b)) are populated with electrons and lie at a higher energy level than the 3p σ bonding orbitals also with t_{1u} symmetry (denoted by t_{1u} (σ^b)). Assuming that allowed 3p–1s transitions can be observed from both 3p bonding orbitals, Dodd and Glen considered that the higher energy peak in the Kβ bands of MgO (see Fig. 9) is assigned to a 3p (π^b)-1s transition, and that the lower energy peak in each band is assigned to a 3p (σ^b)-1s transition. The slightly distorted α-Al_2O_3 octahedra gives a Kβ-band spectrum (see Fig. 3) essentially similar to that of MgO, and the interpretation of the spectrum is considered to be similar. A suggestion drawn from this discussion is that both MgO and α-Al_2O_3 have a surprisingly high degree of covalent character, corresponding to the large contribution of p-π bonding.

Dodd and Glen also gave the tentative MO energy-level diagram for the tetrahedrally coordinated crystalline oxides, as shown in Fig. 10.[13] As with octahedral oxides, the major peak is assigned to a 3p–1s transition. In this case the 3p(σ)-bonding orbitals having t_2 symmetry (denoted by $t_2(\sigma^b)$ in Fig. 10) are the only 3p orbitals populated with electrons. Thus, the major Kβ-band peak for Mg, Al and Si tetrahedral oxides (see Fig. 9, 3 and 6, respectively) is assigned to a 3p(σ^b)-1s transition, although each of the spectra appears distinctly different.

The molecular orbital interpretations mentioned above may give a clue to more

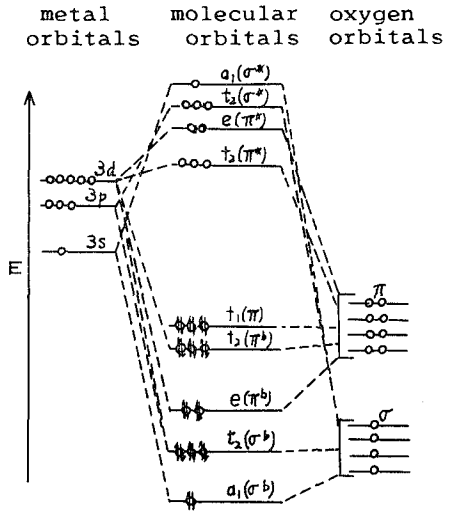

Fig. 10. Molecular-orbital energy-level diagram for tetrahedrally coordinated oxides of Mg, Al and Si (Dodd and Glen).[13]

quantitative theoretical analysis of K emission bands of oxides.

2. Determination of effective charge

An important conclusion drawn from the MO interpretations is that the bond Mg-O or Al-O has much greater covalent character than expected. The degree of covalency is related to the effective charge of atoms (or ions). To estimate the effective charge, x-ray K emission spectra were found powerful.[31] The method consists of comparison of experimentally determined displacement of $K\alpha_{1,2}$-doublet from the atom in a compound, relative to the elemental state, with the value of displacement estimated theoretically for the completely ionized atom. Theoretical estimation of displacement for ionization was attempted by a number of authors.[31,32,34,38]

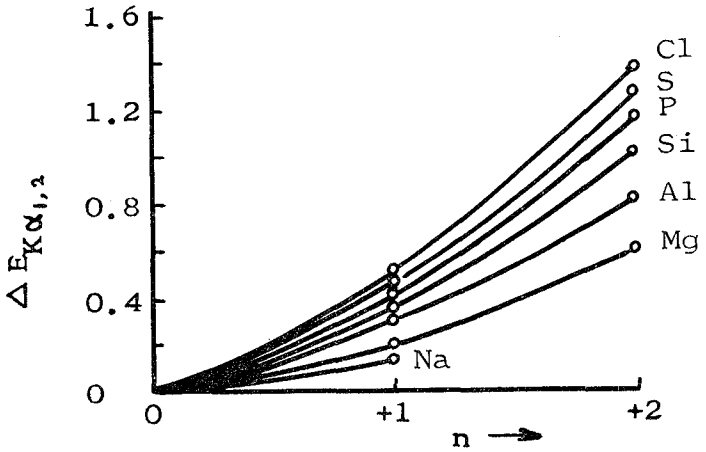

Fig. 11. Shift of $K\alpha_{1,2}$-doublet from the third period elements upon ionization (Urusov).[31]

Table 4 Effective Charges of Si Atoms in Various Silicates Obtained from the Shifts of $K\alpha_{1,2}$-doublet.[31]

Compound	$\Delta E_{K\alpha_{1,2}}$ (ev)	Effective charge
SiO_2 quartz	0.60	1.40
$SiO_2 \cdot n\ H_2O$ opal	0.58	1.38
Na_2SiO_3	0.58	1.38
Mg_2SiO_4 forsterite	0.61	1.42
$ZrSiO_4$ zircon	0.49	1.25
$CaMgSi_2O_6$ diopside	0.55	1.35
Be_3Al_2 (Si_6O_{10}) beryl	0.60	1.40
$Al(SiO_4)$ (F,OH) topaz	0.60	1.40
$KAl_2(AlSi_3O_{10})(OH)_2$ muscovite	0.54	1.34
$CaAl_2(Al_2Si_2O_{10})(OH)_2$ margarite	0.57	1.37
$CaAl_2Si_2O_8$ anorthite	0.54	1.34
$KAlSi_3O_8$ orthoclase	0.57	1.37

Table 5 Effective Charges of a Number of Elements in Silicates[31]

Compound	Element	$\Delta E_{K\alpha_{1,2}}$ (ev)	Effective charge
Na_2SiO_3	Na	0.09	0.85
$MgSiO_3$	Mg	0.18	1.00
$Be_3Al_2(Si_6O_{18})$	Al	0.39	1.20
$KAlSi_3O_8$	〃	0.31	1.02
$CaAl_2Si_2O_8$	〃	0.26	0.90

Figure 11 shows the theoretical displacement $\Delta E\ K\alpha_{1,2}$ for the first two ionization states of the elements of the third period, which was given by Urusov.[31] With this figure the ionization state n corresponding to the experimental value of the displacement can be determined and that value is the effective charge of the atom. The effective charges of Si atom in various silicates calculated from $\Delta EK\alpha_{1,2}$ by Urusov are shown in Table 4. It can be seen from the table that the effective charge of Si atom is not more than $+1.4$ for all the cases examined. It is suggested that the use of the shift of $K\alpha_4$ emission, which is more sensitive to the chemical bonding than that of $K\alpha_{1,2}$, may give more detailed information.[31]

Incidentally, Urusov estimated the effective charge of oxygen in silicates as about -1 by using the effective charges determined by the shift of $K\alpha_{1,2}$-doublet for a number of atoms of the third period (Table 5) and assuming the effective charge of K in $KAlSi_3O_8$ to be unity.

VI. SUGGESTED WORKS

1. General

Much work is left to be done in K-emission spectroscopy. As to measurement, more precision works are necessary. Although many measurements on the shift of emission peak were published, the results obtained by different authors do not agree

with each other so well and a series of data by one author cannot be utilized as supplement by the other author. For example, the shift $\Delta 2\theta$ of AlKα peak from α-Al_2O_3, relative to AlKα peak from Al metal, is 0.095, 0.060, 0.087, 0.100 and 0.082, respectively, according to Brindley and McKinstry,[18] Day and Rindone,[22] Tagai, Iwai and Mori,[19] Terai, Kuroda and Ueno,[17] and Shuvaev, Blokhin and Izrailevich.[21] The present author obtained a value of 0.097 in a very preliminary work. It should be taken into account that all these data were obtained by the identical procedure, that is, x-ray fluorescence method. The above discrepancies demonstrate an urgent necessity of intimate calibration of the instrument.

As to the theoretical interpretation of the K-emission spectra of oxides and silicates, application of molecular orbital theory used by Dodd and Glen[13] seems plausible and its development may be a direction to be taken. Since the theory cannot be applied easily to complex systems and it gives only qualitative explanation at present, however, semiempirical treatment of the quantitative values of, say, peak shift accompanied by precision measurement would be appropriate for the time being.

It should be stressed that when a simple, straightforward "fingerprinting" way is applied for finding, for example, coordination number, other factors such as interatomic distance and effective charge should be checked as all affect the value of peak shift. That is, other factors than coordination have to be taken into account before a definite conclusion is reached. For instance, Shuvaev, Blokhin and Izrailevich[21] have reached the conclusion from the measured value of the shift of AlK$\alpha_{1,2}$ that the coordination number of aluminum in a BaO-Al_2O_3-TiO_2-SiO_2 glass is less than 4. Since their conclusion has been drawn from a simple fingerprinting, more careful re-examination would be necessary before it is confirmed.

2. Glasses

It has been mentioned that x-ray K emission spectroscopy is especially meaningful to glasses. A number of subjects to be studied will be cited:

A) More complete work on the suggested change of Al coordination in a series of glasses with different Al/Na ratio.

B) Structural changes of the environments of Mg, Al and Si with composition in conventional glasses.

C) Short range order, especially, the coordination of Al atoms in special and new glasses.

D) Structure at the sites of other elements (for example, P, S, Ti or Cr) than Mg, Al and Si.

E) High pressure effects on Al sites in glass.

Subject A is re-examination of the works described in the foregoing sections of this review. Subject B is an application of the method utilized by White and Gibbs[24] and Urusov[31] for silicate crystals to silicate glasses. Informations on coordination, effective charge or interatomic distance will give deeper insight into glass structure and contribute to the problem of glass formation. No work has been published yet on this subject. Subject C is similar to subject B. This is a very interesting subject, since special glasses or new glasses may contain Al and other atoms in a coordination state different from in conventional glasses. At present various ways of obtaining glasses

of special composition, such as splat cooling[39] and vapor deposition,[40] are available. Subject D aims at application of the method to non-silicate glasses (phosphate glass, sulfide glass, *etc.*) or glasses containing much amount of transition metal ions (Ti, Cr *etc.*).

Subject E will need a brief explanation. An interesting branch of high pressure works on glass[41,42] is to find how the local structure of glass is subjected to compression. The structure of boron atom site was studied with NMR method by Bray, Kline and Poch,[43] who concluded that no coordination change of boron atom occurred. Boron atom is known to be one of glassnetwork formers and is in threefold or fourfold coordination, depending upon the composition of glass. On the other hand, study on transition metal ions[44] (cobalt or nickel ions) by optical absorption measurement showed that they could change their coordination number upon application of high pressure. Cobalt and nickel are usually considered to be network modifiers. Accordingly, whether aluminum, a typical intermediate ion, changes its coordination number upon application of high pressure or not is of great interest. The AlK emission spectra will be appropriate means for detection of possible change in the coordination state.

VII. CONCLUSION

The current state of x-ray K-emission spectroscopy, particularly as applied to oxides and silicates, has been reviewed. Although the problem of precision in measurement of chemical shift is left to be solved and theoretical interpretation of the spectra is not sufficiently developed, this method is a useful tool for elucidation of short range order in ceramics and glasses. Especially for glasses which have no long range order, the K emission spectroscopy is sometimes the only means to give informations on coordination number, interatomic distance and effective charge of certain constitutents, and many subjects are expected to be studied.

REFERENCES

(1) See, for example: S. Sakka, *Kagaku Kogyo (Chemical Industry)*, **20,** 1525 (1969).
(2) J. Zarzicky, Physics of Non-Crystalline Solids, ed. A. Prince, p. 525, North-Holland (1965); B. E. Warren, *Amer. Ceram. Soc. Bull.*, **46,** 401 (1967).
(3) P. Tarte, Physics of Non-Crystalline Solids, ed. A. Prince, p. 549, North-Holland (1965).
(4) R. F. Tucker, Advances in Glass Technology, p. 103, Plenum Press, New York (1963); H. Imagawa, *J. Non-Crystalline Solids,* **1,** 335 (1969).
(5) P. J. Bray, Interaction of Radiation with Solids, ed. A. Bishay, p. 92, Plenum Press (1967).
(6) W. A. Weyl, Coloured Glasses, Society of Glass Technology, Sheffield (1951); E. Schnitzer, Glass in Electronics, ed. J. D. Mackenzie, Glass Industry (1967).
(7) C. R. Kurkjan and E. A. Sigety, *Phys. Chem. Glasses,* **9,** 73 (1968); G. H. Frischat and G. Tomandl, *Glastech. Ber.,* **42,** 182 (1969).
(8) H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow and P. D. Zemany, X-ray Absorption and Emission in Analytical Chemistry, John Wiley and Sons, New York and London (1960).
(9) L. V. Azàroff, *Science,* **151,** 785 (1966).
(10) K. Nakahara, Methods of Studying Structure of Inorganic Compounds (Experimental Chemistry, New Series, Vol. 6, p. 348, ed. Japan Chemical Society, Maruzen (1965).
(11) N. Uyeda, Experimental Methods of Chemical Analysis Using Instruments, Chapter 6, p. 300, Gikensha, Kyoto (1962).

(12) For example: A. E. Lindth and O. Lundquist, *Ark. Mat. Astr. Fysi.*, **18,** No. 14 (1924).
(13) C. G. Dodd and G. L. Glen, *J. Appl. Phys.*, **39,** 5377 (1968).
(14) V. A. Batyrev and A. V. Shatunova, *Izvest. Akad. Nauk SSSR, Physics Series,* **31,** 883 (1967).
(15) A. Faessler, Soft x-ray Band Spectra and the Electronic Structure of Metals and Materials, ed. D. J. Fabian, p. 93, Academic Press, London and New York (1969).
(16) R. Hayami and H. Wakabayashi, Abstracts of the Papers, 4th Meeting of Glass Division, Japan Ceramic Association, Tokyo, p. 61 (1968).
(17) R. Terai, S. Kuroda and T. Ueno, *Reports Osaka Government Indust. Res. Inst.*, **20,** 172 (1969).
(18) G.W. Brindley and H. A. McKinstry, *J. Amer. Ceram. Soc.*, **44,** 506 (1961).
(19) H. Tagai, T. Iwai and Y. Mori, Abstracts of the Papers, 7th Meeting on Basic Science of Ceramics p. 31, Jan. 28, Tokyo (1969).
(20) D. J. Fabian, Soft x-ray Band Spectra and the Electronic Structure of Metals and Materials, Academic Press, London and New York (1969).
(21) A. T. Shuvaev, M. A. Blokhin and E. A. Izrailevich, *Izvest. Akad. Nauk SSSR, Physics Series,* **31,** 919 (1967).
(22) D. E. Day and G. E. Rindone, *J. Amer. Ceram. Soc.*, **45,** 579 (1962).
(23) E. Cremer, A. Faessler and K. Krmer, *Naturwiss.*, **11,** 377 (1959).
(24) E. W. White and G. V. Gibbs, *Am. Mineral.*, **52,** 985 (1967).
(25) M. A. Blokhin, *Izvest. Akad. Nauk SSSR, Physics Series,* **26,** 429 (1962).
(26) A. T. Shuvaev and G. M. Kulyabin, *Izvest. Akad. Nauk SSSR,* **27,** 322 (1963).
(27) G. W. Brindley and M. Nakahara, *J. Amer. Ceram. Soc.*, **42,** 311 (1959).
(28) J. E. Stanworth, Physical Properties of Glass, Clarendon Press, Oxford (1953); H. Rawson, Inorganic Glass-Forming Systems, Academic Press, London and New York (1967).
(29) D. E. Day and G. E. Rindone, *J. Amer. Ceram. Soc.*, **45,** 490 (1962).
(30) E. D. Lacy, *Phys. Chem. Glasses,* **4,** 234 (1963).
(31) V. S. Urusov, *Geokhimiya,* **No. 4,** 399 (1967).
(32) C. A. Coulson and C. Zauli, *Molec. Phys.*, **6,** 525 (1963).
(33) A. T. Shuvaev, *Izvest. Akad. Nauk SSSR,* **25,** 986 (1961).
(34) A. T. Shuvaev, *Izvest. Akad. Nauk SSSR,* **28,** 758 (1964).
(35) K. Böke, *Z. Phys. Chem., Neue Folge,* **10,** 45 (1957).
(36) L. V. Azàroff, *J. Appl. Phys.*, **38,** 2809 (1967).
(37) G. L. Glen and C. G. Dodd, *J. Appl. Phys.*, **39,** 5372 (1968).
(38) W. Nefedow, *Phys. Status Solidi,* **2,** 904 (1962); See reference 31.
(39) P. T. Sarjeant and R. Roy, *J. Amer. Ceram. Soc.*, **50,** 500 (1967).
(40) J. D. Mackenzie, Modern Aspects of the Vitreous State, Vol. 3, ed. J. D. Mackenzie, p. 149, Butterworths, London (1964).
(41) S. Sakka and J. D. Mackenzie, *J. Non-Crystalline Solids,* **1,** 107 (1969).
(42) M. Tashiro, T. Yamamoto and S. Sakka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45,** 318 (1967).
(43) P. J. Bray, D. Kline and W. Poch, *Glastech. Ber.*, **39,** 175 (1966).
(44) M. Tashiro, T. Yamamoto and S. Sakka, *J. Ceram. Assoc. Japan,* **75,** 202 (1967).